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The role of hydrogen bonds in the melting points of sulfonate-based protic organic salts

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There are three main types of interactions inside organic salts – electrostatic interaction, hydrogen bonding and van der Waals force [1−4]. While van der Waals force is relatively weak, it is hydrogen bonding and particularly electrostatic interaction that determine the lattice energies of ionic systems and other physicochemical properties like melting points [5]. The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X−H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation [6]. Hydrogen bonds in the solid state fall into the classification of strong, moderate, and weak hydrogen bonds [7]. In *molecular systems* like H_2O (*vs.* H_2S) or NH_3 (*vs.* PH_3), strong hydrogen bonds lead to higher melting points. However, in organic salts, the situation may be different [8,9].

In this presentation, we will present our important discovery on the influence of hydrogen bonding on the melting points of sulfonate-based protic organic salts [9]. We found five pairs, among which we will discuss in detail results of two highly similar *protic organic salts* – 1,2,4-triazolium methanesulfonate and imidazolium methanesulfonate. Both of them are solid-state proton conductors. The electrostatic interaction energy was calculated based on the single crystal X-ray and neutron diffraction data, showing that 1,2,4-triazolium methanesulfonate has higher electrostatic interaction energy at various temperatures. Moreover, variable-temperature infrared spectra, deuterium isotope effects, and singe crystal data indicate much stronger hydrogen bonding inside 1,2,4-triazolium methanesulfonate. Therefore, 1,2,4-triazolium methanesulfonate is expected to have a higher melting point than imidazolium methanesulfonate. However, surprisingly, 1,2,4-triazolium methanesulfonate exhibits a much lower melting point (134 °C) than imidazolium methanesulfonate (188 °C). Therefore, it is concluded that stronger hydrogen bonding inside 1,2,4-triazolium methanesulfonate results in a much lower melting point than imidazolium methanesulfonate.

References

[1] T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
[2] A. Matic and B. Scrosati, *MRS Bull*., 2013, **38**, 533.
[3] H. Weingärtner, *Angew. Chem., Int. Ed*., 2008, **47**, 654.
[4] R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *Angew. Chem. Int. Ed.*, 2013, **52**, 4623.
[5] L. Glasser, *Inorg. Chem.*, 2012, **51**, 2420.
[6] E. Arunan, G. R. Desiraju, R. A Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, and D. J. Nesbitt , *Pure Appl. Chem.*, 2011, **83**, 1637.
[7] T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.
[8] A. Wulf, K. Fumino and R. Ludwig, *Angew. Chem., Int. Ed.*, 2010, **49**, 449.
[9] J. Luo *et al*., manuscripts in preparation.